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THE OXIDATION, IGNITION AND DETONATION OF FUEL VAPORS AND GASES

III. THE CAUSE OF THE EFFECT OF METALLIC DOPE TO DELAY DETONATION[1]

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Abstract

The antiknock effect of metallic dope is attributed to the catalytic action of the surface, maintained in an oxidizing atmosphere by continuous deposition thereon of the metal of the dope, to oxidize the fuel in part to steam and carbon dioxide, the consequent dilution of the end gas causing a reduction of inflammability sufficient to prevent completion of combustion in other than the normal manner. Experiments indicate that temperatures required for the necessary catalytic activity are attained during the period of flame travel; not prior to ignition. In support of the theory experimental evidence is given showing that, (*a*) steam is especially effective to reduce inflammability, (*b*) doped pentane or hexane oxidizes without ignition to steam and carbon dioxide only in reaction chamber No. 10, described in Part I, at any temperature of reaction, (*c*) the carbon dioxide–steam reaction is inhibited by a sulphur catalyst poison and the similar action in the engine destroys the antiknock effect of the dope. It is shown further by experiments with and without additions of a catalyst poison to *undoped* engine fuel that, in conditions leading to high surface temperatures in the combustion space, a carbon dioxide–steam reaction having a considerable antiknock effect is obtained. The engine experiments with catalyst poisons are completed by obtaining conditions in which tetraethyl lead becomes a pro-knock. It is recognized that the catalyst theory depends fundamentally on the oxidation of hydrocarbon fuel being a heterogeneous reaction as indicated by the experiments described in Part II, and some further evidence in support of the view, obtained by using catalyst poisons, is given in this Part.

Introduction

The discovery by Midgley and Boyd of the remarkable effect of tetraethyl lead present in extremely small concentration in engine fuel, to delay the onset of detonation as the compression ratio is raised, was followed by a spate of explanatory theories, the number extending ultimately to more than a dozen. Those proposed prior to 1926 and reviewed by Clark and Thee (5) did not involve a departure from accepted belief concerning the mechanism of the oxidation of the paraffin hydrocarbons present in large proportion in normal engine fuel and mainly responsible for the occurrence of detonation.

Such a departure was made in the Callendar nuclear drop–peroxide theory (3, 4) submitted to the Aeronautical Research Committee, December, 1926, in that oxidation was taken to begin with the formation of an organic peroxide instead of an hydroxyl compound as required by the generally accepted, Armstrong–Bone hydroxalation theory. Support was afforded the peroxide theory by the work of Moureu, Dufraisse, and Chaux who followed Callendar in associating peroxides with fuel detonation (15).

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Egerton and Gates (6), in a review of the theories of antiknock action, agreed that peroxides, acting as autocatalysts, are formed in the early stage of combustion and suggested that metallic antiknocks form comparatively stable peroxides which react with and destroy the fuel peroxides which are then regenerated. The suggestion led Egerton (7, pp. 2911–2926) to the formulation of a chain reaction theory in which peroxide is an essential link, the development of the reaction to cause knocking being interrupted on the destruction of the peroxide by the metal of the dope, which is oxidized in the process. Finally, Beatty and Edgar (2, pp. 2927–2936) in a comprehensive review of the theory of knock in internal combustion engines conclude that "antiknock agents act as inhibitors for the slow oxidation reactions in the end gas. Their effect is to break short the reaction chains and so prevent the chain development from reaching that critical point at which its multiplication begins".

Theories that antiknocks act by destroying organic peroxides or by breaking reaction chains in an homogeneous fuel–air mixture are not accepted but discussion can be reserved. The reviews mentioned do, however, deal with two matters related to experimental work described in Parts I (8) and II (9) and later in this Part.

Beatty and Edgar mention particularly the difficulty of relating oxidation as it occurs in laboratory experiments to the similar effect in the end gas of an engine. Thus it is stated that laboratory oxidations cannot be carried to temperatures higher than 500° C. because of the incidence of ignition or explosion, and that time of reaction is sometimes 1000-fold greater than in an engine. The statements were, of course, made before the development of reaction chamber No. 10, described in Part I (8) in which it is possible to carry laboratory oxidations of hydrocarbons commonly used as engine fuel to whatever temperature is required for completion, 700° C. or over, without ignition and in reaction times of a second or less.

The positive catalyst theory, which assumes that antiknocks accelerate oxidation *prior to ignition* in the engine and accordingly weaken the mixture to an extent sufficient to prevent detonation, is mentioned by Egerton with the comment that the antiknocks retard oxidation and consequently the theory is contrary to fact. Beatty and Edgar also mention the theory and dismiss it on sounder grounds by observing, in effect, that promotion of the oxidation of the fuel by antiknocks during the *early stages of combustion* in an engine is not in accordance with experimental facts.

Revised Positive Catalyst Theory

The experiments described in Part I (8) and others to be described in this Part show that the oxidation of paraffin hydrocarbons doped with iron carbonyl, in reaction chamber No. 10, which provides conditions approaching those obtaining in the combustion space of an engine, is a heterogeneous reaction on a surface of iron maintained as such in an oxidizing atmosphere by continuous deposition of metal from the organic compound. The final

products only, namely steam and carbon dioxide, are produced at any temperature of reaction. The reaction does not proceed with high velocity until surface temperature exceeds 500° C. Such high surface temperatures would be found in the combustion space of an engine on the exhaust valves in conditions of maximum power output and momentarily on other surface exposed to radiation from the advancing flame which reaches temperatures of 2500° C. and over, depending on compression ratio and other factors. The end gas in which detonation occurs is heated by compression to temperatures of 650° C. and over, depending on compression ratio, and would be expected to attain even higher temperatures because of turbulence. Temperature and turbulence conditions are, therefore, as required to promote extremely rapid surface oxidation of the doped fuel to final products which could reduce the inflammability of the end gas to such an extent that completion of combustion would be possible solely by normal flame travel. An adequate explanation for the antiknock action of metallic dopes is then obtained without having to determine the cause of detonation.

Section I

Effect of Steam to Reduce Inflammability

The effect of steam, nitrogen, and carbon dioxide as diluents on the inflammability of a normal fuel–air mixture used in the E 35 engine was determined by Ricardo (17). The work was extended and the experimental results discussed some time later by Alcock (1). The gases mentioned were added to the fuel–air charge in increasing proportion until inflammability was so reduced that misfiring occurred. It was emphasized that elaborate precautions, including superheating, were required to ensure that steam was added to the engine charge as such, not as part water.

It was found that 8.9% of steam sufficed to reduce inflammability to the extent required to cause misfiring although flame temperature was reduced by 125° C. only. Carbon dioxide was required in the proportion of 19.6% to produce a similar effect although flame temperature was reduced by 400° C. The conclusion was that steam exerted a nonthermal effect to reduce inflammability, the nature being unknown. Whatever the nature of the effect may be, the magnitude is of great importance, and from the data given above it is calculated that, on a weight basis, steam is six times more effective than carbon dioxide, the other product of the complete combustion of hydrocarbons.

Effect of Steam to Reduce the Inflammability of Hydrogen

Hydrogen is especially suitable for experiments to determine the effect on inflammability of steam which is the sole final product of oxidation. It was mentioned, Part I (8), that tetraethyl lead and iron carbonyl had been shown by Mardles to promote the oxidation of hydrogen. The rate of oxidation was not, however, related to inflammability, and the experiment using the carbonyl as the oxidant has been repeated in carefully controlled

conditions and using a conventional flow method. The combustion tube was of silica, 1 in. internal diameter, supported in a vertical 6 in. furnace. Silica was selected because of its relatively inactive surface. The hydrogen and air were from high pressure cylinders and, therefore, nearly dry, but, as a further precaution, the gases were passed over phosphorus pentoxide while en route to the combustion tube. The reacting mixture was supplied at the rate of 200 cc. per min. and contained hydrogen in the concentration of 40% by volume. Iron carbonyl, as vapor, was added to the air stream at the rate of 40 mgm. per hour. Temperatures were taken by means of a thermocouple in a silica sheath placed at the position of maximum temperature on the longitudinal axis of the combustion tube. The hot gases from the combustion tube were passed through a Liebig condenser and then through a U-tube

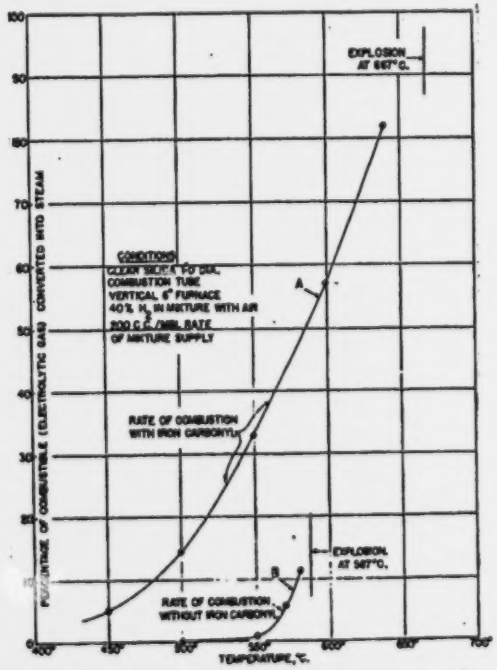

FIG. 1. *Graphs showing the effect of steam from a heterogeneous reaction to reduce inflammability and thereby raise explosion temperature.*

containing calcium chloride. Rates of oxidation were measured by weighing the water of combustion at suitable time intervals. When iron carbonyl was added to the reacting mixture, iron oxide was deposited on the tube at the positions of the upper and lower convection circulation, see Fig. 5, Part I (8), and in view of the fact that the mixture contained both oxidizing and reducing

gases, care was taken that the equilibrium oxide had formed prior to measuring rate of combustion. Equilibrium was taken as having been established at a particular temperature when water of combustion was obtained at a constant rate.

Graph *A* of Fig. 1 gives rates of steam formation when the hydrogen–air mixture contained the vapor of iron carbonyl, and Graph *B*, rates of steam formation when the mixture without the vapor was passed through the tube in clean condition. It will be noted that with iron carbonyl present combustion of electrolytic gas occurred at the easily measurable rate of 5%, at 450° C., whereas the rate was about 1% only at 550° C., in the absence of the carbonyl and 33-fold greater when it was present. The mixture containing iron carbonyl exploded at 667° C. and at 587° C., in the absence of the carbonyl.

Concluding Comments

The experiments by Ricardo and Alcock show the effect of steam from an outside source to reduce the inflammability of the reacting mixture in an engine. Those just described show a similar effect obtained by steam produced by the reaction itself.

Section II

The Oxidation of Pentane in Reaction Chamber No. 10, as Affected by Iron Carbonyl

The reaction chamber was described in Part I (8), and experiments on the effect of flow configuration described in Part II (9) indicated that oxidation in the chamber is a heterogeneous reaction so far as doped pentane is concerned and probably of a similar character in respect of pentane alone. Experiments described in this section were made to confirm the earlier results and to determine the effect on rate of oxidation of changing the concentration of iron carbonyl and the effect of a residual surface of iron oxide.

The experimental results shown by the graphs of Figs. 7, 8, 9 and 10 of Part I (8) were obtained immediately after the completion of the reaction chamber. The chamber was then dismantled, cleaned with hydrofluoric acid, washed with steam, and an oxidation of pentane containing iron carbony in the concentration of 0.5% repeated. The experimental results are plotted on Graph *B* of Fig. 2, together with those obtained earlier, and it will be noted that the two sets of results fall on a single curve showing a degree of repeatability not generally obtained when using conventional methods.

The increase in rate of reaction obtained on doubling the dope concentration is shown by Graphs *B* and *C* of Fig. 2. A useful comparison can be made at the temperature of 550° C., when about half of the oxygen remained uncombined. The increase was from 4.1 to 5.5 moles of oxygen reacted, that is, 30%. Flow configuration was similar for both experiments and the increase is attributed to some possible increase in the area of the effective catalytic iron surface or to an increase in the density of the catalyst.

Rates of formation of carbon oxides for the smaller concentration of iron carbonyl were given by the graphs of Fig. 8, Part I (8). Exactly similar results were obtained when using the larger concentration and as before reaction was substantially to steam and carbon dioxide whatever the temperature.

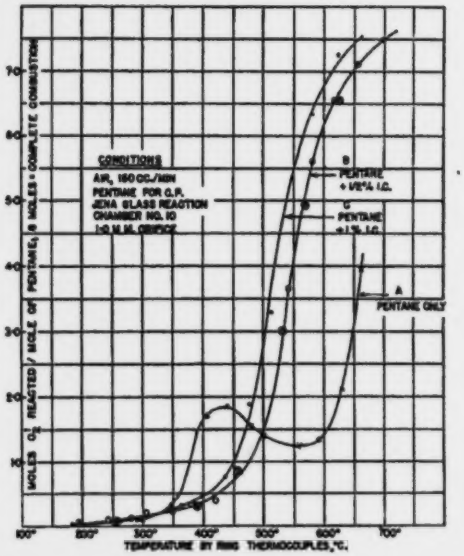

FIG. 2. *Graphs showing the increase in velocity of the carbon dioxide–steam reaction due to doubling the iron carbonyl concentration in pentane.*

Pentane Oxidation on Residual Oxide Surface

The coating of the surface of the reaction chamber with iron and iron oxides seen after oxidation of pentane doped with iron carbonyl was shown, *B*, Fig. 6 of Part I (8); distribution varies with rate of mixture supply and the concentration of iron carbonyl in the pentane and thickness with time of use of the doped pentane, but the surface becomes completely coated with brick red oxide on continued use of the chamber with undoped mixture. The results of an oxidation of pentane after use of the chamber with pentane containing iron carbonyl in the concentration of 1.0% are given by Graph *C* of Fig. 3. Graph *A* for pentane oxidized in the chamber when clean and Graph *B* for the oxidation of pentane plus 1.0% iron carbonyl are given for ease of comparison. The graphs show that when the metal surface was no longer maintained by continuous deposition from the carbonyl, rates of reaction at temperatures above 500° C. are greatly reduced and tend to approach those obtained when the reaction chamber surface is clean glass. Thus at 550° C. rate of reaction fell from 5.2 moles, Graph *B*, to 1.8 moles of oxygen reacted, Graph *C*. At 625° C., oxygen was reacted at the rate of

7.25 moles when using the doped mixture, Graph *B*, but diminished to 5.8 moles for the residual surface, Graph *C*, and further to 4.6 moles after 3½ hr., as shown by the single observation marked with an arrow below Graph *C* of the figure.

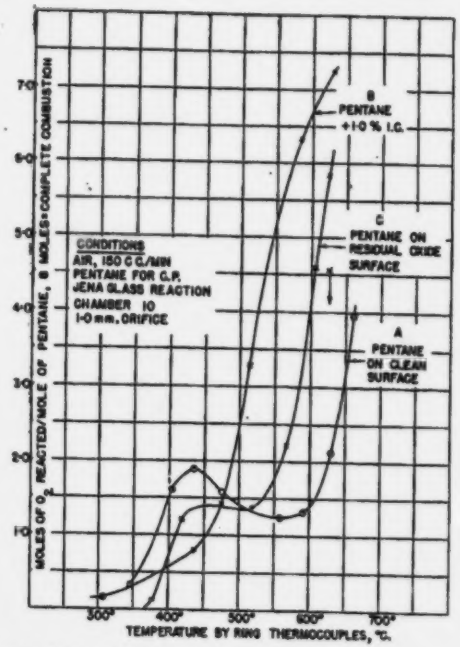

FIG. 3. *Graphs showing the effects on the oxidation of pentane of ceasing to maintain the catalytic surface provided by continuous deposition of iron from the carbonyl.*

The reappearance of the aldehyde hump, Graph *C* of Fig. 3 when the active metal surface of the reaction chamber surface was converted to oxide is of great interest and supports the view, expressed in Section V of Part II (9), that the oxidation of pentane to partial products, including aldehyde, is a heterogeneous reaction.

Section III

THE OXIDATION OF HEXANE IN REACTION CHAMBER NO. 10, AS AFFECTED BY IRON CARBONYL

Hexane is present in considerable proportion in normal engine fuel and is of relatively low octane number. Experimental results for the effect of metallic antiknocks on the oxidation of the substance, hitherto published, have always been obtained by conventional methods and because of the almost complete oxidizing nature of combustible mixtures with air, reaction could not occur on a surface of metal deposited from the dope, except at very

low temperatures. The consequent effect of the dope to inhibit the oxidation of hexane and higher paraffins in the same circumstances is the experimental basis of current theory attributing the antiknock action to an antioxidant property. It became of special interest, therefore, to determine if the oxidation of hexane in reaction chamber No. 10 at high temperatures would be promoted on the addition of metallic dope and if reaction would be to final products as for pentane oxidation.

Oxidations in Reaction Chamber No. 10

The experimental conditions were as described for oxidations of pentane. The 'hexane', supplied by the Anglo-American Oil Company, was procured from the fractional distillation of nearly aromatic-free petroleum spirit. The density was 0.6965, and distillation range 62° to 85° C. for a 95% fraction.

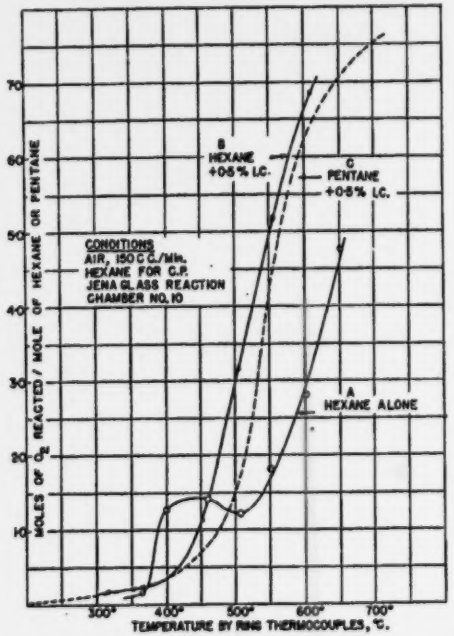

FIG. 4. *Graphs showing the effect of iron carbonyl to promote the oxidation of hexane at high temperatures as compared with the similar effect for pentane.*

Experimental results are given by the graphs of Fig. 4: Graph *A* is for hexane alone in the reaction chamber in clean condition; Graph *B* is for hexane plus iron carbonyl in the concentration of 0.5%. The combining proportions mixtures used for the experiments were made up on the assumption that the hexane was normal and that 9½ moles of oxygen would be required accordingly

for the complete oxidation of one mole of the paraffin. It will be noted that the characteristics of hexane oxidation are similar to those determined for the oxidation of pentane. Graph *C* of the figure, for the oxidation of doped pentane, is reproduced from Fig. 2 and appears to show that iron carbonyl possesses the greater oxidation promoting effect in respect of pentane, but, when allowance is made for the specific oxygen consumption, the carbonyl is found to be of equal effect in respect of the two paraffins, as nearly as can be determined without exact knowledge of molecular composition.

The oxidation of doped hexane was, as for doped pentane, substantially to steam and carbon dioxide at any temperature of reaction, as shown by the graphs of Fig. 5.

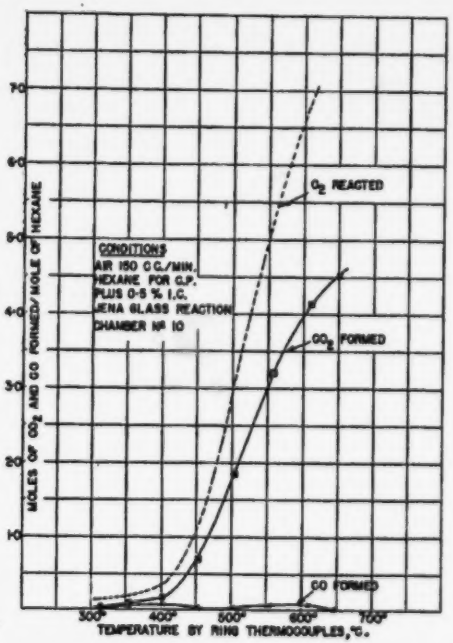

FIG. 5. *Graphs showing that the oxidation of hexane containing iron carbonyl is substantially to carbon dioxide and steam at all temperatures of reaction.*

Section IV

THE SPECIFIC EFFECT OF ETHYL MERCAPTAN TO INHIBIT THE HETEROGENEOUS REACTION OF PENTANE AND HEXANE TO STEAM AND CARBON DIOXIDE

Having shown that the antiknock, iron carbonyl, suppresses the formation of partial oxidation products, including aldehyde, and promotes the formation of steam and carbon dioxide at all temperatures of reaction, it remains to

determine which of the two effects is responsible for the antiknock property of the carbonyl. The use of a catalyst poison in oxidation and related engine experiments makes it possible to distinguish between the effects mentioned.

Ethyl Mercaptan and Hydrogen Sulphide

The one hydrogen atom of the mercaptan and the two of the sulphide are replaceable by metal. Either substance converts a contact surface of iron to one of iron sulphide and is without effect on a surface of iron oxide. Both substances were known from earlier experiments to destroy the antiknock effect of the metallic dopes. The mercaptan, rather than hydrogen sulphide, was used for laboratory experiments to avoid the complications involved in the supply and measurement of the sulphide at the small rates required. The concentration of 2.5% by weight of the mercaptan in the pentane and hexane is without significance except that in engine experiments it was sufficient to destroy the antiknock effect of 2 cc. per gal.* of tetraethyl lead in an engine fuel.

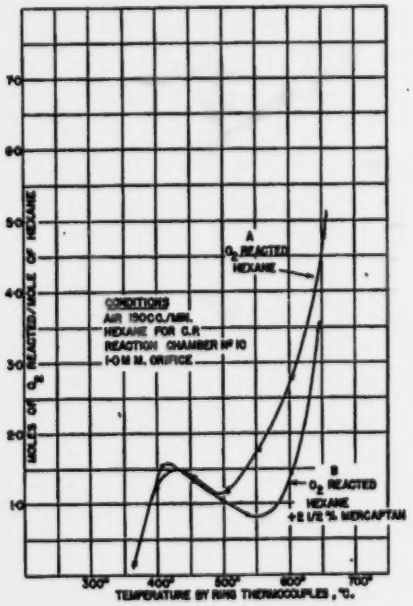

FIG. 6. *Graphs showing that ethyl mercaptan, a catalyst poison, does not affect the aldehyde reaction in a glass reaction chamber (No. 10).*

Effect of Ethyl Mercaptan on the Oxidation of Hexane in Reaction Chamber No. 10

The experimental results are given by the graphs of Figs. 6, 7, and 8. It is of special significance, as shown by the graphs of Fig. 6 for oxygen reacted,

* *References throughout this paper are to the imperial gallon.*

that the mercaptan had no measurable effect on reaction velocities at temperatures below about 480° C., that is, at the temperatures of the formation of partial products including aldehyde. The inhibitory effect was confined to the carbon dioxide–steam reaction as shown by the graphs of Figs. 7 and 8 for rates of formation of carbon oxides.

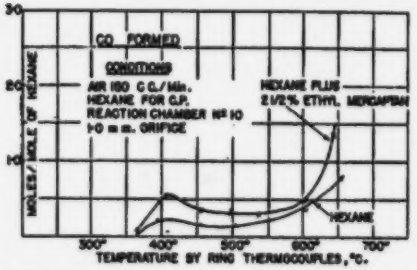

FIG. 7. *Graphs showing the effect of ethyl mercaptan on carbon monoxide formation when hexane is oxidized in reaction chamber No. 10.*

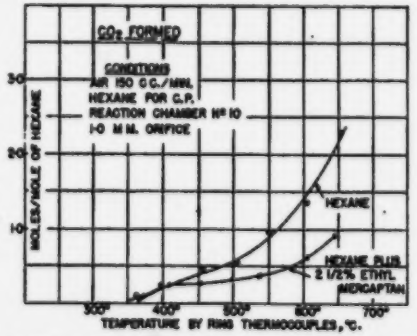

FIG. 8. *Graphs showing the effect of ethyl mercaptan on carbon dioxide formation when hexane is oxidized in reaction chamber No. 10.*

Effect of Ethyl Mercaptan on the Oxidation of Hexane plus Iron Carbonyl in Reaction Chamber No. 10

The experimental results are given by the graphs of Figs. 9, 10, and 11. At 550° C. oxygen was reacted at the rate of 5.0 moles when the pentane contained 0.5% of iron carbonyl, Graph *A*, Fig. 9. The rate was 1.2 moles only when the doped pentane contained 2½% of mercaptan. Carbon dioxide, at the same temperature, was formed at the rate of 1.75 moles without the mercaptan and 0.25 moles with it. Carbon monoxide formation, Fig. 11, was inappreciable in either case. At 600° C. oxygen reacted was 6.6 moles without the mercaptan and 0.8 moles with it. There was a corresponding change in rate of carbon dioxide formation, and carbon monoxide formation occurred at an appreciable rate, 0.25 moles.

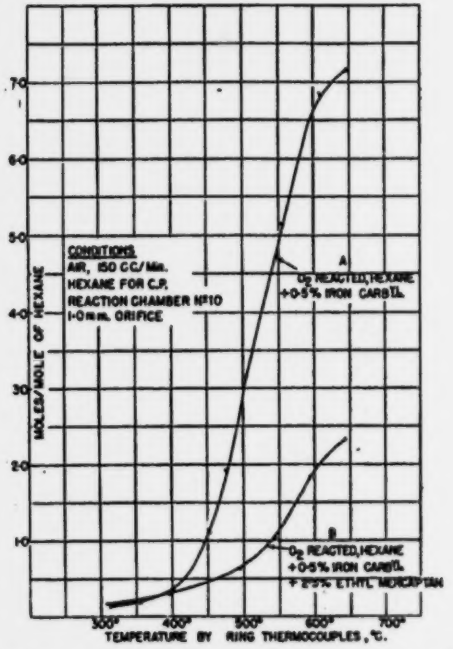

FIG. 9. *Graphs showing the inhibiting effect of ethyl mercaptan on the oxidation of hexane doped with iron carbonyl in glass reaction chamber (No. 10).*

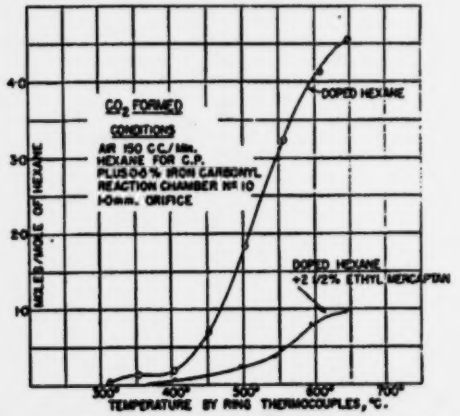

FIG. 10. *Graphs showing the effect of ethyl mercaptan on carbon dioxide formation when doped hexane is oxidized in glass reaction chamber (No. 10).*

The Effect of Ethyl Mercaptan on the Oxidation of Pentane in Reaction Chamber B, Fig. 11, Part II (9)

The reaction chamber was of mild steel which does not rust uniformly. The surface in contact with the reacting mixture of pentane–air would, therefore, comprise areas of iron oxide which would promote the formation of

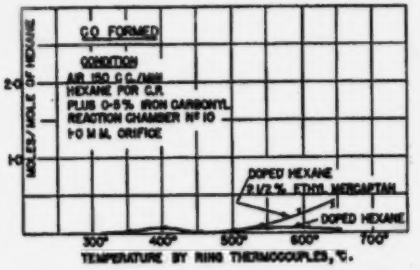

FIG. 11. *Graphs showing the effect of ethyl mercaptan on carbon monoxide formation when doped hexane is oxidized in glass reaction chamber (No. 10).*

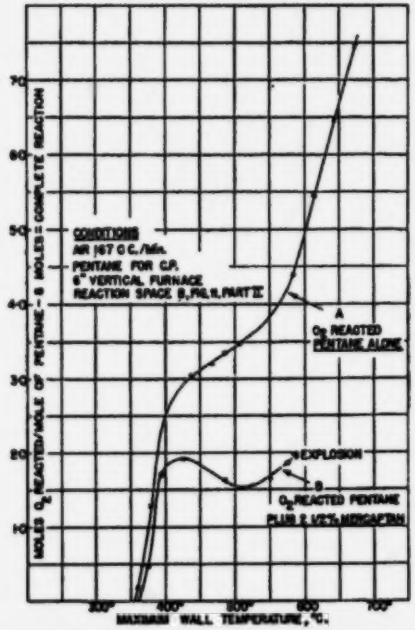

FIG. 12. *Graphs showing the effect of ethyl mercaptan on the oxidation of pentane (undoped) in a steel reaction chamber.*

partial oxidation products and areas of iron which would promote oxidation to final products, and, as there existed a steep temperature gradient over the length of the chamber, reaction can occur at a range of temperatures even when the maximum is 600° C. or over. The mixed nature of the reaction in the chamber is shown by Graph *A* of Fig. 12, which is characteristic of both the aldehyde and the carbon dioxide–steam reactions. The effect of the mercaptan is shown by Graph *B* of the figure. The carbon dioxide–steam reaction is nearly eliminated, as shown by the graphs of Figs. 13 and 14, leaving the aldehyde, which, in the absence of dilution with steam and carbon dioxide, ignites and explodes when the temperature reaches 590° C.

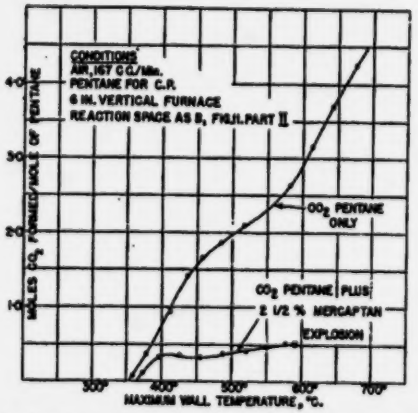

FIG. 13. *Graphs showing the effect of ethyl mercaptan on carbon dioxide formation when pentane is oxidized in the steel reaction chamber.*

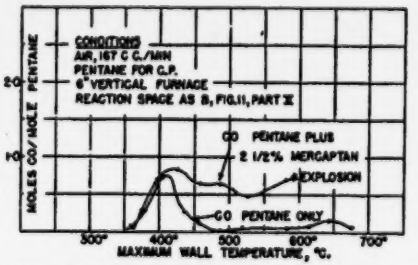

FIG. 14. *Graphs showing the effect of ethyl mercaptan on carbon monoxide formation when pentane is oxidized in the steel reaction chamber.*

Pentane Oxidation on Surface Remaining after the use of Mercaptan

An oxidation of pentane in the steel reaction space, as above, was carried out after the oxidation of pentane plus the mercaptan. The experimental

results are given by the graphs of Fig. 15 and show a considerable residual effect. Thus, for example, at 550° C., 3.8 moles of oxygen were reacted when the reaction chamber was first used. The rate dropped to 1.7 moles (Fig. 12) when the mercaptan was present and rose to 2.3 moles only on the residual surface (Fig. 15). The rates of carbon monoxide and carbon dioxide formation

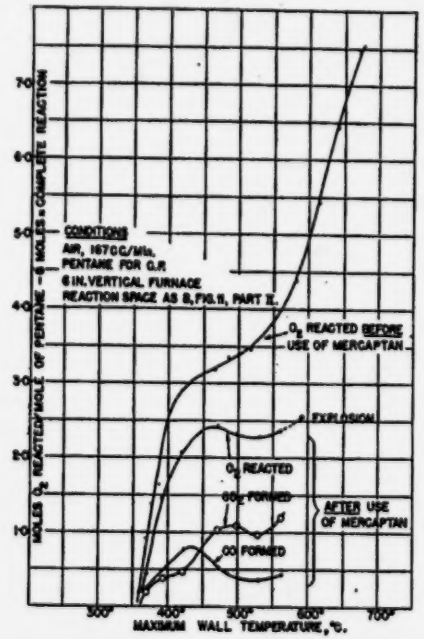

FIG. 15. *Graphs showing the effect of the surface of iron sulphide remaining after the use of ethyl mercaptan on the oxidation of pentane in the steel reaction chamber.*

on the residual surface are given by the lower graphs of Fig. 15 and comparing them with the graphs of Figs. 13 and 14 for pentane plus the mercaptan it will be seen that change of rates of carbon dioxide and carbon monoxide formation is in accordance with the changes in rates of oxygen reacted.

Conclusions

The experiments described in this section help to confirm that the oxidation of pentane is a heterogeneous reaction and show definitely that it is possible by the use of a catalyst poison to determine whether the antiknock action of metallic dope is due to the effect to inhibit the aldehyde reaction or the effect to promote reaction to final products.

Section V

The Pro-knock Effects of Lubricating Oils, Ethyl Mercaptan, and Hydrogen Sulphide

An extensive series of experiments, made some years ago by King and Moss (10, 11, 13, 14) demonstrated that lubricating oils when added to engine fuel varied in pro-knock effect. The greatest effect was obtained when the oils were added to doped fuels. Olein or oleic acid in a concentration of 1.0% only in the fuel destroyed almost the entire antiknock effect of nickel carbonyl in the large concentration of 10 cc. per gal. in the fuel, and was of similar effect in respect of iron carbonyl, but a concentration of 12% of olein in the fuel was required to destroy 85% of the antiknock effect of a 12 cc. per gal. addition to the fuel of tetraethyl lead. Castor oil, which is soluble in engine fuel to the extent of about 1½% only, was as effective as olein in destroying the antiknock value of nickel carbonyl, somewhat less effective in respect of iron carbonyl but was found to be of no *antiknock* effect when added to fuel doped with tetraethyl lead. The effect of the rape oils which are soluble in any concentration was similar to that of castor. The mineral oils were quite effective in reducing the antiknock value of the carbonyls but large additions were required in respect of tetraethyl lead even to obtain a relatively small effect.

The variation of the pro-knock effect with the natures of the oils and the metals of the dopes could not be explained in terms of theories based on homogeneous reactions, and little information was available about the effect of the several oils on heterogeneous reactions when the contact surfaces were of iron, nickel, or lead. It was known, however, that olein or oleic acid is a poison in respect of nickel catalysts (18, p. 909). Comment was made accordingly in the published account of the experiments and no further explanation attempted.

Similar engine experiments were made later using ethyl mercaptan and hydrogen sulphide additions to engine fuel instead of lubricating oils. The substances, added in small proportion, destroyed completely the antiknock effects of tetraethyl lead and iron carbonyl and gave rise to further pro-knock effects which will be described later. Again the experimental results could not be explained by accepted theory. The sulphur compounds were known catalyst poisons in respect of the carbon dioxide–steam reaction on iron and nickel surfaces, but an explanation of their pro-knock effect given accordingly would have involved the assumptions that catalytic surfaces were provided in the combustion space by the metallic dopes and that the steam formed on them in the absence of a catalytic poison was responsible for the antiknock effect. The experimental results were, therefore, withheld from publication until experiments could be made on the oxidation of hydrocarbon engine fuel at the high temperature of the 'end gas' and on the effect of sulphur catalyst poisons on the reactions.

Selection of Sulphur Catalyst Poison

It was a convenience to use a liquid compound soluble in engine fuel, and thiophene, carbon disulphide, and ethyl mercaptan were tried. The pro-knock effects of the compounds on straight run aviation petrol doped with 2.0 cc. per gal. of tetraethyl lead when used in the C.F.R. engine with unheated induction, are shown by the graphs of Fig. 16. It will be seen that all three

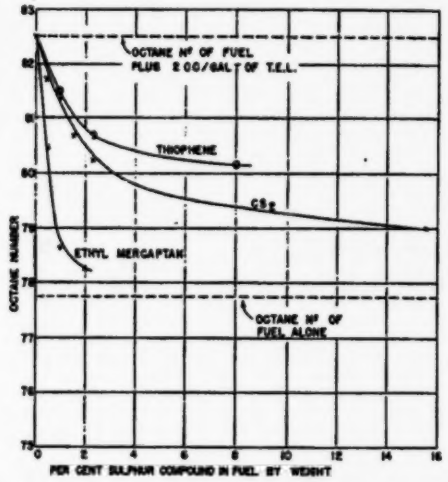
OCTANE Nº OF FUEL PLUS 2 CC/GAL OF T.E.L.
THIOPHENE
CS2
ETHYL MERCAPTAN
OCTANE Nº OF FUEL ALONE
OCTANE NUMBER
PER CENT SULPHUR COMPOUND IN FUEL BY WEIGHT

FIG. 16. *Graphs showing the pro-knock effect of three sulphur compounds when added to a low octane number engine fuel doped with tetraethyl lead. C.F.R. engine.*

substances were pro-knocks and that the mercaptan was outstanding, a concentration of 2% in the fuel being sufficient to destroy nearly all of the effect of tetraethyl lead to raise the octane number of the fuel from 77.8 to 82.5. It was not possible to prevent the loathsome odor of the mercaptan from reaching many parts of the building in which the engine was situated, and hydrogen sulphide was used as an equivalent catalyst poison for further experiments.

Engine Experimental Conditions

The experiments were made with a variety of hydrocarbon fuels used in the C.F.R. research engine. The intake air was unheated in some cases and in others raised to 300° F. as required for the standard method of determining octane number. The knocking tendency of the fuels was generally obtained by the H.U.C.R. method as used in the Air Ministry Laboratory (12), but sometimes by determining octane number. Some experiments were, however, made with very weak or very rich mixtures. Tetraethyl lead was used as the fuel dope in preference to iron carbonyl which on long continued use, especially in large concentration, destroys spark plug insulation and leaves

heavy deposits of oxide in the engine combustion space. The engine experimental results are given by a series of graphs and the experiments are described in succeeding paragraphs.

Hexane Experiments

Experiments with hexane as an engine fuel are of special interest because of the oxidation experiments described in Sections III and IV. The experiments were made with increasing additions of hydrogen sulphide when using either hexane alone or hexane plus 8.0 cc. of tetraethyl lead per gallon and when using correct, rich, and weak mixtures and heated and unheated air supply.

The experimental results are shown by a series of graphs, Fig. 17, H.U.C.R. being plotted against hydrogen sulphide additions. Mixture strengths are

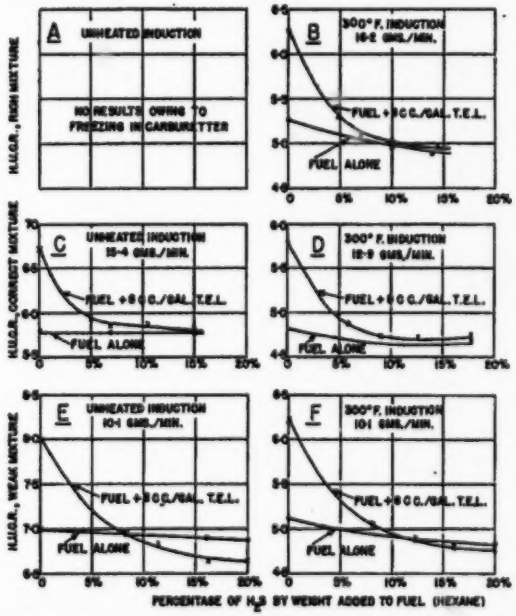

FIG. 17. *Graphs showing the pro-knock effect of hydrogen sulphide in respect of hexane doped with tetraethyl lead. C.F.R. engine, for correct, rich, and weak mixtures and heated (300° F.) and unheated induction.*

shown by the figures for fuel consumption in grams per minute. Considering first the results for correct mixture strength, Graphs *C* and *D*, it will be seen that with unheated induction, Graph *C*, H.U.C.R. increased from 5.75 to 6.7 on adding the dope to the pentane and then diminished to 5.9 when hydrogen sulphide was added in the concentration of 5%, that is, 85% of the antiknock

value of the dope addition was destroyed. On increasing the hydrogen sulphide addition even to the large concentration of 15% of the weight of the fuel, nothing more happened than the complete destruction of the antiknock effect of the metallic dope.

The engine would not run on hexane at high compression ratios without excessive detonation unless the mixture were very weak or very rich, and results of experiments made accordingly and with heated or unheated induction are given by the Graphs *B*, *E*, and *F* of Fig. 17. The graphs show that by using the hexane at a relatively high compression ratio or with a high induction temperature a small pro-knock effect in respect of the undoped fuel is obtained on adding hydrogen sulphide to the mixture. The explanation advanced is that in conditions of high inlet temperature and high flame temperature due to high compression ratio, the exhaust valve and/or other not well cooled surfaces, such as the piston crown, are raised to the temperature required for the partial oxidation of the end gas to steam and carbon dioxide. The temperature is about 400° C. according to the experiments with a steel reaction chamber, see Fig. 12, and on inhibition of the reaction by hydrogen sulphide the pro-knock effect shown by the experiments would be expected.

A further interesting effect is shown by Graphs *E* and *F*, fig. 17. The graphs cross, showing that the hydrogen sulphide after destroying the antiknock effect of the dope and that due to oxidation of the fuel on hot surfaces carries on to give rise to a further pro-knock effect. The 'further' effect increases as the compression ratio is raised and flame temperature increased accordingly. This will be discussed in succeeding paragraphs.

Aviation Fuel Experiments

The fuel was a high grade straight run Borneo petrol and when used undoped and with *unheated* induction the catalyst poisons were without the pro-knock effect which became evident when metallic dope was added. The experimental results given by the graphs of Fig. 18, obtained with an *induction temperature of 300° F.*, show the double effect already mentioned, that is, the hydrogen sulphide not only destroys the entire antiknock effect of the metallic dope but also the smaller similar effect attributed to the formation of steam and carbon dioxide on combustion chamber surfaces becoming active in the high temperature conditions. The two pro-knock effects obtained on adding hydrogen sulphide in a concentration of about 8% in the fuel suffice to reduce the octane number to 64.5.

Coal Spirit Experiments

The spirit was procured from the low temperature distillation of coal. The octane number was higher than that of the petrol but lead response was less; a 4 cc. per gal. addition of the metallic dope raised the octane number from 75½ to 84, whereas a similar addition to the aviation petrol raised the octane number from 70 to 85. The relatively low concentration of 3% of the hydrogen sulphide was sufficient to destroy the original antiknock effect of the dope, represented by an increase of 8½ octane numbers. The second and third

effects are as described for the engine experiments with hexane but are of greater magnitude and obtained with smaller percentages of hydrogen sulphide.

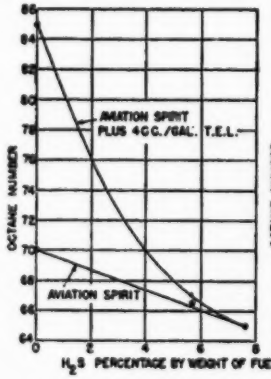

FIG. 18.

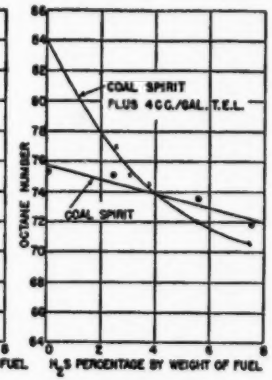

FIG. 19.

FIG. 18. *Graphs showing the pro-knock effect of hydrogen sulphide on aviation spirit doped with tetraethyl lead. C.F.R. engine, 300° F. induction temperature.*

FIG. 19. *Graphs showing the pro-knock effect of hydrogen sulphide on coal spirit doped with tetraethyl lead. C.F.R. engine, 300° F. induction temperature.*

Cyclohexane Experiments

The second and third pro-knock effects of hydrogen sulphide are shown by the engine experiments already described to become increasingly evident as the temperature of combustion is raised either by increasing compression ratio or by raising induction temperature. The experiments were, therefore, repeated in conditions requiring the use of compression ratios approaching the limit of the C.F.R. engine. Weak and rich mixtures of cyclohexane were used with induction temperatures of 300° F. and it will be seen by reference to the graphs of Fig. 20 that the highest useful compression ratios were 7.9 and 7.4 respectively in the circumstances. The H.U.C.R. values increased to 10.0 and 9.1 on adding tetraethyl lead to the fuel in the concentration of 24 cc. per gal. The excessive dope addition was used advisedly in an endeavor to determine whether the third pro-knock effect shown by the crossing of the graphs was due to the hydrogen sulphide or to the metallic dope in the presence of the sulphide. It is well known that the specific effect of tetraethyl lead diminishes as the concentration in engine fuel increases and it is probable that no more than one-third of the 24 cc. addition was effective to prevent detonation. The experimental results given by the graphs of Fig. 20 show that (*a*) The original increase in H.U.C.R. due to the dope was destroyed by about 5% of hydrogen sulphide in the weak mixture and about 2½% in the rich mixture.

(*b*) The second pro-knock effect of the hydrogen sulphide is more pronounced than in the experiments made at lower compression ratios. Thus the sulphide

in the concentration of 15% reduced the H.U.C.R. of the undoped fuel, weak mixture, from 7.9 to 6.2, that is, an amount equal to 80% of the increase obtained with the large addition of dope to the fuel in the absence of the catalyst poison. Similar effects were obtained for the rich mixture but comparisons cannot be made because the percentage of hydrogen sulphide added to the fuel–air mixture was not large enough to obtain limiting values for the effects.

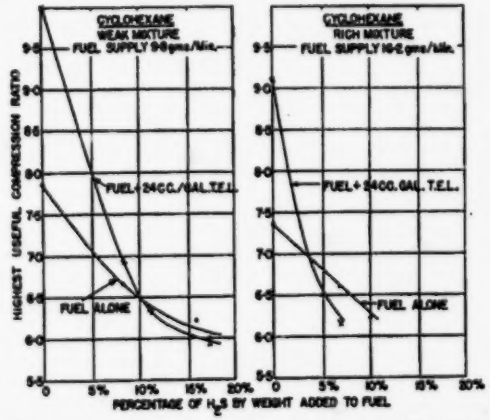

FIG. 20. *Graphs showing the pro-knock effect of hydrogen sulphide on rich and weak mixtures. Cyclohexane doped with tetraethyl lead. C.F.R. engine, 300° F. induction temperature.*

(*c*) The third pro-knock effect of the hydrogen sulphide, shown by the crossing of the graphs, is most apparent for the rich mixture for which fuel was supplied at the rate of 16.2 gm. per min. as compared with 9.8 for the weak mixture. The rich mixture in the engine contained, therefore, nearly twice as much dope as the weak mixture, and, since conditions in respect of hydrogen sulphide supply remained unchanged, it is reasonable to suppose that the third pro-knock effect was due in some way to the tetraethyl lead when used at high flame temperatures in the presence of the sulphide.

Benzene Experiments

The experiments with benzene as the engine fuel were undertaken to confirm that, as suggested above, tetraethyl lead becomes a pro-knock if used in conditions of high flame temperature and in the presence of hydrogen sulphide. It is well known that benzene does not detonate in the C.F.R. engine even when the compression ratio is as high as 10. The addition of metallic dope is, therefore, without apparent effect. Experiments were made accordingly at an induction temperature of 300° F. The experimental results are given by the graphs of Fig. 21. They show that when the undoped fuel was used at the high compression ratio of 10, detonation did not occur until hydrogen sulphide had been added to the mixture in the high concentration of nearly 20% by

weight of the benzene. This result confirms that the 'further' pro-knock effect observed in the earlier experiments was not due to the effect of the hydrogen sulphide alone. It will be noted, however, that on adding tetraethyl lead to the benzene in the concentration of 4 cc. per gal. detonation occurred

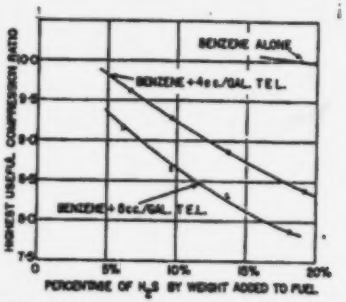
BENZENE ALONE
BENZENE + 4 c.c./GAL. T.E.L.
BENZENE + 8 c.c./GAL. T.E.L.
HIGHEST USEFUL COMPRESSION RATIO
PERCENTAGE OF H_2S BY WEIGHT ADDED TO FUEL

FIG. 21. *Graphs showing the pro-knock effect of tetraethyl lead in small concentration in benzene obtained when combustion occurs in the presence of hydrogen sulphide. C.F.R. engine, unheated induction.*

and the H.U.C.R. fell to 9.6 when the percentage of hydrogen sulphide in the fuel was 7% only, and further to 8.4 when the percentage was increased to 19. On increasing the concentration of tetraethyl lead to 8 cc. per gallon, a still greater pro-knock effect was obtained as shown by the lower graph of the figure, H.U.C.R. being reduced to 9.1 when the percentage of hydrogen sulphide was about 7, and to 7.8 when it was 18.

Section VI

Discussion of Experimental Results

Nature of the Reactions Described

It was suggested, Section V, Part II (9), for discussion and further experiment "that the oxidation of pentane is an heterogeneous reaction, velocity depending on the nature of the contact surface and the manner in which the reacting mixture is brought into contact with it". Some further experimental work supporting the general proposition has been described in this Part and will be discussed in succeeding paragraphs.

When pentane is oxidized in reaction chamber No. 10, and the active surface is of clean Jena glass, the usual aldehyde hump appears on the graph for oxygen reacted, see Fig. 3. If now iron carbonyl be added to the reacting mixture, giving an active surface of iron, the aldehyde hump disappears and reaction is almost completely to steam and carbon dioxide (Graph *B* of the figure). Then on allowing the active surface to go to iron oxide by ceasing to supply the carbonyl, the aldehyde hump reappears (Graph *C* of the figure). These experimental results obtained with a flow configuration especially adapted rapidly

to remove oxidation products from the surface on which they are formed give strong support to the view that the oxidation reaction is heterogeneous.

The experiments with ethyl mercaptan give further support to the view mentioned. Thus, the graphs of Fig. 6 for the oxidation of hexane in the glass reaction chamber No. 10 in clean condition show that the aldehyde hump remains when ethyl mercaptan is added to the reacting mixture, indicating that the mercaptan is without effect to alter the surface at the temperature of the experiments. If, however, iron carbonyl be added to the reacting mixture instead of the mercaptan, Fig. 9, and an active surface of iron is deposited on the glass, the aldehyde hump disappears, and oxidation is to carbon dioxide and steam at all temperatures of reaction, as for pentane in similar conditions. If now the active iron surface is converted to the sulphide on adding the mercaptan, the aldehyde hump is not recovered and reaction velocity at all temperatures diminishes to a relatively low rate. The rate may reach zero at temperatures rising to over 500° C. and be inappreciable at higher temperatures in *suitable conditions of flow configuration* as shown by Graph *B*, Fig. 18, Part II (8). Again it is difficult to interpret the experimental results otherwise than by considering the reactions to be heterogeneous.

The experiments with the steel reaction chamber of relatively large volume, Fig. 12, are also significant. The surface was not of uniform temperature and was in part of iron oxide and in part of iron. The oxidation of pentane in the chamber is, therefore, a mixed reaction yielding, over the low temperature range, aldehyde on the oxide and final products on the iron. On adding ethyl mercaptan to the mixture, the reaction to aldehyde which occurs on the surface of iron oxide as previously shown, Fig. 3, continues but that to steam and carbon dioxide occurring on the iron part of the surface is inhibited, giving the over-all result as shown by the graphs of Fig. 12.

The Negative Temperature Coefficient of Reaction

The negative coefficient depends for its existence on the aldehyde hump which is more pronounced for oxidations in reaction chamber No. 10 than for oxidations in conventional combustion reaction spaces. It is necessary, therefore, in seeking an explanation to remember that in reaction Chamber No. 10 oxidation occurs with great rapidity, time of exposure being of the order of one second, that the high velocity of reaction is due to the flow configuration being adapted to remove surface oxidation products immediately on their formation, that the products do not remain in the chamber and on leaving it to reach the exit are exposed to temperatures lower than that of their formation. The chamber is thus suitable for following the course of reactions occurring at specified temperatures, and the existence of a negative temperature coefficient when pentane is oxidized in the chamber on other than a metal surface indicates that a reaction of high velocity is succeeded, on raising the temperature, by one of lower velocity. Thus referring to the graphs of Fig. 10, Part I (8), it will be seen that carbon monoxide formation reaches a maximum at about 400° C., the temperature of the aldehyde hump,

and then falls to a minimum at 520° C. The rate of carbon monoxide formation then rises as temperature increases, slowly at first but with great rapidity at temperatures above 600° C. until at 660° C. it exceeds that of carbon dioxide formation. The experimental results show a high reaction velocity over the lower temperature range when the pentane is oxidized to aldehyde, and initially a relatively low reaction velocity at higher temperatures when the pentane is oxidized to carbon monoxide. During the temperature interval between the high velocity, low temperature reaction to aldehyde and the acceleration to high velocity of the high temperature reaction to carbon monoxide, the over-all rate of oxygen reacted reaches the relatively low value which accounts for the negative temperature coefficient. The oxidation of pentane could not proceed in the manner described if the reactions were homogeneous, so conversely the existence of a negative temperature coefficient may be taken as an indication of heterogeneous reactions.

A negative temperature coefficient of reaction was obtained by Pease (16) nearly 20 years ago and was observed when propane was oxidized by a flow method. The experiments of Pease and those of later workers are discussed by Jost in *Explosion and Combustion Processes in Gases*, pages 427–449, English translation by Huber O. Croft, and it is stated, page 449, that many facts support the conclusion that the reaction mechanism differs as between low and high temperature.

Oxidation in the End Gas in an Engine

If oxidation of the fuel in the end gas be a heterogeneous reaction, the antiknock effect of metallic dope can be attributed to catalytic action, and detonation in the body of the gas cannot be due primarily to any process of oxidation. If, on the other hand, oxidation be a homogeneous reaction, existing theory in respect of the cause of detonation and the antiknock action of metallic dope would be supported. Antiknock action only will be discussed at present although some of the experimental work described in Parts I (8) and II (9) has an important bearing on the cause of ignition and detonation; a subject which it is proposed to discuss in a subsequent Part.

The Revised Positive Catalyst Theory

It is well established that the unburned combustible mixture (end gas) confined between the advancing flame and some part of the surface of the engine combustion space is the seat of detonation, that the *metal* of organometallic compounds is responsible for their antidetonation effect, and that turbulence is effective to reduce detonation. The temperature of the end gas in an engine not supercharged and using unheated mixture has been calculated to increase from 670° C. for a compression ratio of 4 to 880° C. for a compression ratio of 10, while the flame temperature may rise accordingly from 2500° to 2750° C., and radiation would be expected to give rise momentarily to high surface temperatures. The conditions as described, although prevailing for a small fraction of a second, suffice for at least partial oxidation of the end gas by flameless combustion. The experimental results for the

laboratory oxidation of doped pentane or hexane given by the graphs of Fig. 8, Part I (8), and Fig. 5 of this Part, in conditions of temperature, turbulence, and time of reaction approaching those prevailing in the combustion space of an engine, show that the metal of the dope deposited on the available surface effects the oxidation of the hydrocarbons to steam and carbon dioxide with great rapidity at temperatures above 500° C., as long as the metal surface is maintained by continuous deposition from the organometallic compound. The end gas in an engine is always at a temperature higher than 500° C. late in the period of flame travel and the contact surface of the gas probably at a still higher temperature due to radiation from the flame. Doped fuel in the end gas would, in the circumstances, be oxidized with great rapidity to steam and carbon dioxide on the catalytic surface maintained as in the laboratory reaction chamber by continuous deposition of the metal of the dope. The effect of steam especially to reduce inflammability is shown by the experiments described in Section I, and, dilution of the end gas being sufficient, self-ignition ahead of the flame could not occur and combustion would be completed in the normal course without detonation. Verification that the action of metallic dope is as described is obtained by considering the effects of sulphur compounds which are catalytic poisons in respect of the carbon dioxide – steam reaction on metal surfaces. Thus, ethyl mercaptan inhibits the carbon dioxide–steam reaction in laboratory oxidations of doped fuels, as shown by the experiments described in Section IV, and the mercaptan or hydrogen sulphide, when added to doped engine fuel, destroys the antiknock effect of the organometallic compounds as shown by the experiments described in Section V. When hexane undoped was used as fuel in the C.F.R. engine in conditions leading to relatively low flame and engine temperatures, the catalytic poison was of no pro-knock effect even in the large concentration of 15% in the fuel, Graph *C*, Fig. 17. However, when conditions of engine operation led to relatively high surface temperatures in the combustion space, the consequent steam–carbon dioxide reaction became an antiknock factor because knock occurs on its inhibition by the catalyst poison (see Figs. 18, 19 and 20). The antiknock effect of hot surfaces is most evident at high compression ratios which are necessarily accompanied by correspondingly high flame temperatures. Thus, referring to Fig. 20, inspection of the graphs shows the decrease in H.U.C.R. obtainable by inhibition of the carbon dioxide–steam reaction to be almost as great as the increase obtained on the addition of tetraethyl lead in very large concentration. That is, the tetraethyl lead antiknock effect is added to an existing effect. Both effects are due to dilution of the end gas with the product of a carbon dioxide–steam reaction and both are destroyed by the catalyst poison.

Acknowledgments

In addition to the acknowledgments made in Part I, in respect of the experimental work carried out in the Colloid Science Laboratory, Cambridge, thanks are due to Dr. George Mole for assistance with the experiments on

the oxidation and ignition of hydrogen described in Section I and to Dr. H. Moss and Mr. W. J. Stern for assistance with the engine experiments described in Section V.

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